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Dispersive liquid–liquid microextraction for the determination of phenols by acetonitrile stacking coupled with sweeping-micellar electrokinetic chromatography with large-volume injection

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ABSTRACT

The current routes to couple dispersive liquid–liquid microextraction (DLLME) with capillary electrophoresis (CE) are evaporation of water immiscible extractants and backextraction of analytes. The former is not applicable to extractants with high boiling points, the latter being effective only for acidic or basic analytes, both of which limit the further application of DLLME-CE. In this study, with 1-octanol as a model DLLME extractant and six phenols as model analytes, a novel method based on acetonitrile stacking and sweeping is proposed to accomplish large-volume injection of 1-octanol diluted with a solvent–saline mixture before micellar electrokinetic chromatography. Brij-35 and β-cyclodextrin were employed as pseudostationary phases for sweeping and also for improving the compatibility of sample zone and aqueous running buffer. A short solvent–saline plug was used to offset the adverse effect of the water immiscible extractant on focusing efficiency. The key parameters affecting separation and concentration were systematically optimized; the effect of Brij-35 and 1-octanol on focusing mechanism was discussed. Under the optimized conditions, with ~30-fold concentration enrichment by DLLME, the diluted extractant (8×) was then injected into the capillary with a length of 21 cm (42% of the total length), which yielded the overall improvements in sensitivity of 170–460. Limits of detection and qualification ranged from 0.2 to 1.0 ng/mL and 1.0 to 3.4 g/mL, respectively. Acceptable repeatability lower than 3.0% for migration time and 9.0% for peak areas were obtained. The developed method was successfully applied for analysis of the phenol pollutants in real water samples.

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1. Introduction

Since its inception in 2006 [1], dispersive liquid–liquid microextraction (DLLME) has attracted much attention due to simplicity of operation, low solvent usage and cost, high enrichment efficiency and very short extraction time compared to other liquid phase microextraction techniques (LPME) [2]. It has been widely applied in determining analytes at trace levels in environmental, food and biological samples [3]. In recent years the commonly used DLLME extractants, such as halogenated hydrocarbons and aromatic hydrocarbons are gradually being replaced by low toxic ones, typically ionic liquids (ILs) [4] and low-density organic solvents [5].

DLLME is mainly linked up with gas chromatography (GC) because water-immiscible extractants are volatile in GC. For high-performance liquid chromatography (HPLC), the extractants are either injected directly or evaporated to dryness before reconstitution and injection, which depends on their compatibility with the mobile phase. Capillary electrophoresis is a powerful complementary technique to GC and HPLC. Its combination with DLLME is regarded as a very attractive environmentally sustainable analytical tool and should have broad application prospects since both of them consume very small amount of organic solvents. However, due to the incompatibility of water immiscible extractants and aqueous background electrolytes (BGEs), the implementation of DLLME with CE has been somewhat slower to develop.

A recent review summarized the use of microextraction combined with CE in bio-analysis [6]. For DLLME, the main mediate routines to couple with CE are evaporation of immiscible extractants [7–13] and backextraction of analytes [14–18]. However, some problems lying in these two methods limit their application.

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Extraction solvents are evaporated under the air or nitrogen steam followed by reconstitution of analytes into an aqueous solution before injection. That requires much time and brings some loss to volatile and semi-volatile compounds, and is not applicable to the extractants with high boiling points including ionic liquid (ILs) and long-chain alkanols. On the other hand, DLLME followed by back-extraction exists to transfer analytes from extraction solvents to aqueous solutions primarily according to the changes in hydrophobic characteristics after ionization. Nevertheless, it is impracticable for neutral analytes and less effective for hydrophobic and ionizable compounds, such as pentachlorophenol [19]. Recently, formation of a microemulsion of the DLLME extractant (chloroform) with an aqueous methanol (MeOH) allowed analytes to be introduced directly into the capillary through electrokinetic injection (EKI) [20]. Whereas, the inherent shortcomings of EKI could not be easily overcome, e.g., discriminatory sample loading amounts, unsatisfactory reproducibility, and for uncharged analytes, the effectiveness is inhibited despite the inclusion of them in ionic micelles [21].

Apparently, these drawbacks can be removed via hydrodynamic injection of immiscible extractants containing target analytes, but in fact it is not easy to combine direct injection of DLLME extractants with capillary zone electrophoresis (CZE) or micellar electrokinetic chromatography (MEKC) coupled with common on-line concentration strategies, such as stacking [22–24], SDS-sweeping [25,26] and stacking with reverse migrating micelles [27]. The problem of incompatibility between DLLME extractants and sample solutions/BGEs required by the on-line concentration techniques remains unsolved.

Notably, an on-line enrichment technique—transient "pseudo-isotachophoresis (p-ITP)", better known as "acetonitrile (ACN) stacking", has several distinctive characteristics compared with others [28,29]. For instance, (i) ca. 66% ACN and high amount of NaCl added into a sample matrix induce isotachophoresis focus for charged analytes, (ii) rapid completion of the enrichment process quickly removes the ionized analytes into the buffer solution, which detaches them from the sample zone avoiding serious influence on the subsequent separation and detection of the analytes, and (iii) it allows large-volume injection of the sample matrix to achieve a high enrichment factor (EF). Inspired by its unique merits, we came up with the following idea. A large proportion of ACN in the sample matrix produces on-line stacking, and could enable water immiscible DLLME extractants to be dissolved and directly introduced into a CE system. In addition, the loss of DLLME EF due to the dilution could be compensated by large-volume sample injection. In this context, it would be a practical and feasible approach to combine DLLME with CE by use of ACN stacking.

In this study, with 1-octanol as a model DLLME extractant and six phenols as model analytes, a novel method based on ACN stacking and sweeping was proposed to accomplish large-volume injection of 1-octanol diluted with a solvent–saline mixture before micellar electrokinetic chromatography. A solvent–saline plug and a buffer containing Brij-35 and β-cyclodextrin (β-CD) were used to counteract the deleterious effect of 1-octanol on stacking and improve the compatibility of the sample zone and aqueous buffer. Parameters affecting the separation and stacking efficiency were systematically optimized to achieve the best analytical performance. Once validated, the method was successfully applied for analysis of these phenols in real water samples.

2. Experimental

2.1. Chemicals

Analytical standards of 2,4,6-trichlorophenol (2,4,6-TCP, 98%), 2,4-dichlorophenol (2,4-DCP, 98%), 2,5-dichlorophenol (2,5-DCP, 98%), bisphenol A (BPA, 99.8%), 4-chlorophenol (4-CP, 99%), 3-methylphenol (3-MP, 99%) were purchased from Aladdin Chemistry (Shanghai, China). Hydrochloric acid, sodium hydroxide, sodium tetraborate and β-CD were provided by Bodi Chemical Reagent (Tianjin, China). NaCl was obtained from Xilong Chemical Reagent (Shantou, China). Sodium dodecyl sulfate (SDS) was obtained from Sanland (Los Angeles CA, USA). Brij-35, Tween-20, cetyltrimethylammonium bromide (CTAB) and 1-octanol (99.5% pure) were purchased from Aladdin Chemistry (Shanghai, China). All reagents were of analytical grade unless indicated otherwise. HPLC-grade MeOH (≥99.9% pure), ACN (≥99.9% pure) and isopropanol (≥99.9% pure) were purchased from Kermel Chemical Reagent (Tianjin, China). Standard stock solutions of the phenols at concentration of 2 mg/mL were prepared in MeOH and stored in brown bottles at −18 °C. A mixed standard stock solution of six phenols was prepared with MeOH at the concentration of 200 μg/mL. Working standard solutions were prepared daily by diluting the mixed stock standard solution with MeOH to the required concentrations.

2.2. Apparatus and conditions

All electrophoresis experiments were performed on a Beckman P/ACE^{TM} MDQ Capillary Electrophoresis System (Beckman coulter, Fullerton, CA) equipped with a photodiode array detector (PAD). Data acquisition and instrument control were carried out using 32 Karat software (Version 8.0, Beckman Coulter). ANOVA was performed using SPSS software (Version 19.0, IBM). Uncoated fused-silica capillaries (50 cm × 50 μm I.D. or 50 cm × 75 μm I.D., with an effective length of 40 cm) were purchased from Ruifeng Optical Fiber Factory (Yongnian, Hebei Province, China). The detector wavelength was operated at 214 nm for optimization of separation, and the wavelength used for quantitative analysis was set at 214 nm for 2,4,6-TCP, 4-CP and 3-MP and 254 nm for 2,4-DCP, 2,5-DCP and BPA. 214 nm, 206 nm and 254 nm were used to evaluate the purity of the phenols in real samples. Electrophoretic separations were carried out with an applied voltage of 20 kV (75 μm I.D.) or 28 kV (50 μm I.D.) under normal polarity. All operations were carried out at 25 °C. The pH values of BGE solutions were adjusted by a pH meter (HANNA Instrument, Italy). Water was purified using a Millipore Direct-Q 3 system (Millipore Corporation, Bedford, MA, USA).

New capillaries were rinsed at 20 psi successively with MeOH for 8 min, water for 3 min, 0.1 M HCl for 5 min, water for 3 min, 0.1 M NaOH for 30 min, water for 5 min, and finally with the running buffer for 20 min and equilibrated at 20 kV with running buffer for 10 min. Between runs, the capillary was rinsed at 20 psi sequentially with the mixture of MeOH and water (1:1, v/v) for 1 min, 0.1 M NaOH for 2 min, water for 1 min and the running buffer for 3 min. All solutions were prepared freshly everyday, submitted to ultrasonic treatment for 5 min and filtered through a cellulose acetate filter (0.22 μm).

In ACN stacking and sweeping-MEKC, the capillary was first conditioned with the BGE consisting of 10 mM β-CD, 40 mM Brij-35 and 10% MeOH in 25 mM borate buffer (pH 11.2). Then the extractant (1-octanol) obtained from DLLME step diluted (8×) in a 100 mM NaCl solution containing 8% (v/v) MeOH and 54% (v/v) ACN was directly injected into the capillary at 3 psi for 40 s (75 μm I.D.), immediately, followed by injection of the solvent–saline plug at 0.5 psi for 10 s. A voltage of 20 kV was then applied for both sample stacking and subsequent separation. With a sample injection at 0.5 psi for 3 s, the sample and the BGE used for conventional MEKC procedure was the same as in the ACN stacking and sweeping-MEKC.

2.3. Sample preparation

Three environmental water samples were collected from the Huaqing pool (Xian, Shaanxi), the Weihei river (Xian, Shaanxi) and

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